

# Composite Boards from Isocyanate Bonded Pine Needles

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**ABSTRACT:** The effect of alkali treatment on the wettability of pine needles was assessed by contact angle measurements. The lower critical surface energy of the treated needle (42%) favors its superior wetting behavior over the control. The composite boards were prepared from these treated needle furnishes and isocyanate prepolymer resin adhesive (3–20%). The results indicate that internal bond strength, modulus of rupture, tensile strength, and screw withdrawal load increased with the increase of resin adhesive content. At lower humidity, the boards with varying resin adhesive contents exhibited 2–7% thickness swelling at equilibrium moisture content whereas at higher humidity, the thickness swelling in the boards ranged between 13–23%. Under immersed water, the composite boards swelled 2–3 times as much as the samples

exposed at 98% RH. After aging, the internal bond strength of boards was reduced by 41–67% in accelerated water and 54–78% in cyclic exposure respectively. Fractographic evidences such as pulled out of needle fibers, fiber fracture and debonding, because of swelling of fibers in the aged samples could be used to explain the loss of strength. The screw withdrawal load of the high resin adhesive content boards (20%) was comparable with the natural wood. The developed composite board satisfies the requirements of Standard Specification: IS: 3087-2005 / EN 312-2003. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3477–3489, 2010

**Key words:** pine needles; isocyanate prepolymer; adhesion; swelling; microstructure

## INTRODUCTION

In recent years, use of nonwoody materials such as agricultural residues and forest wastes for making panel products<sup>1–8</sup> has become more attractive because of ligno-cellulosic similarity to wood particles and also limited wood supply. Several attempts have been made on bonding of these lignocellulosics with commonly used formaldehyde based condensates<sup>2,5,6</sup> and isocyanate resin adhesive<sup>2–4</sup> to produce specification grade particle/ fiber boards. It has been shown that wide variations in the nature and density of agro/forest residues, moisture content of flakes/chips and resin binder flow, and penetration and spread rate significantly affect the properties of boards. The boards made from isocyanate adhesives exhibited improved porosity and water resistance to those bonded with either urea or phenolic resins.<sup>9</sup> However, the main limitation of isocyanate bonded boards is their tendency to adhere to the caul plates and press parts.<sup>10,11</sup> This adhesion can damage the boards and subsequent clean-up of the contaminated platens is difficult and time-consuming. This situation necessitates the use of a self-releasing type of isocyanate based binders during pressing operation to eliminate

their sticking from platens and produce boards of acceptable properties such as surface heterogeneity, strength, and dimensional stability.

In earlier studies,<sup>12–16</sup> utilization of pine needles has been reported as a principal raw material in the manufacturing of particle boards, hard boards, and biocomposites because of their renewableness and huge availability in the Western part of Himalayas. In these, it was shown that boards fail to meet the performance requirements mentioned in Code/Specification set forth by National Organizations.<sup>13–15</sup> Because of waxy coating, needle furnish does not present an easy surface for bonding of adhesives such as urea formaldehyde, phenol formaldehyde, and urea resin-isocyanate resin blend. The resin coverage on the interior of needle will be nonexistent causing weak internal bond strength and high-thickness swelling of the resultant boards. In the case of urea resin-isocyanate blend,<sup>17</sup> rapid reaction between the isocyanate groups and water takes place, because of alkaline properties of urea. This results in a very narrow processing latitude and poor stability of binder. Improvement in these properties of boards could be achieved by pretreatment of pine needles and also by using their blend with other fibers such as bamboo, wood residues, and other ligno cellulosics. Pine needles (40 wt %) bonded with magnesium oxychloride cement was also reported for use as a thermal insulation boards (density <0.4 g cm<sup>-3</sup>).<sup>18</sup> In previous work, isocyanate based binders have not received much attention for

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bonding of the pine needle furnish. Therefore, an understanding on this binder will be required in terms of tolerance of high-flake moisture content, surface absorptivity, low-resin application, press precure time to maintain superior performance, and quality of the panel products.

In this study, we aimed at discussing the use of prepolymer based on a diphenyl methane diisocyanate (MDI) as a binder in the pine needle boards. The effectiveness of this binder is expected mainly, because of its high cross-linking and increased plasticity (better spreading rate on the surface of needle furnish), which results in improved strength and durability of the boards. Using isocyanate prepolymer not only to provide superior adhesive characteristics but also minimizing unwanted adhesion to the platens used in the board manufacturing when compared with conventional polyisocyanates. This could help to increase usefulness of pine needles as a constituent of panel products to be used as wood substitutes in buildings. In this article, we report the properties of composite boards made with various percentage of isocyanate prepolymer bonding agent. Dimensional changes in the boards are recorded as a function of humidity and immersed water conditions. The internal bond strength of boards is discussed in terms of their cohesive microstructural failure under both aged and unaged conditions. The suitability of composite boards is also assessed with requirements of the existing Standard Specification.

## EXPERIMENTAL

### Materials

The pine needles of 300–380 mm length were collected from the Indian forests (density,  $0.22 \text{ g cm}^{-3}$ ; moisture content,  $\sim 20\%$ ; water absorption,  $\sim 45\%$ ). The needles were comprised of cellulose (40–43%), hemicellulose (20–24%), lignin (36–40%), extractives (25–28%), and ash content (2–4%). Aromatic polyisocyanate prepolymer was obtained from M/s Bayer Material Science, Germany (Desmodur E 23, NCO content,  $15.4 \pm 0.4\%$ ; viscosity,  $1800 \pm 250 \text{ mPa}\cdot\text{s}$ ; density,  $1.13 \text{ g cm}^{-3}$ ). The pull-off adhesive strength of this prepolymer is 0.61 MPa when tested as per ASTM D 4541. Under peel adhesion, the lattice squares are intact satisfying the 5 B criteria of ASTM D 3359. The single-lap joint shear strength is 12.37 MPa tested as per ASTM D 1002. Commercial grade sodium hydroxide was used for digestion of the pine needles. Paraffin wax (m.p.  $60^\circ\text{C}$ ) was procured from M/s Fine Organics, Mumbai (India).

### Sample preparation

Pine needles were cut to a desired length (30 mm). Thereafter, they were digested with 2% aqueous sodium hydroxide solution (wt % of needles) as optimized in

earlier work.<sup>19</sup> The treated mass was washed with running water to remove its extractives and residual alkali. The initial weight loss in the pine needles was 15% after treatment. Subsequently, the samples were dried at  $103 \pm 2^\circ\text{C}$  to a constant moisture content and hammer milled to an average furnish size of  $\sim 2 \text{ mm}$ .

The needle furnishes were placed in a rotary drum blender and treated them by spray application of isocyanate prepolymer resin adhesive. The binder level is ranged between 3–20 wt % of furnish. This range is selected because board manufacturing industries are usually applied resin adhesives to a level of 15–18 wt % for bonding of lignocellulosic particles to maintain their economical viability. It is also noted that above 20 wt % resin adhesive content, the excess of adhesive is squeezed out from the sides of molds during pressing. The treated mass was then placed on the bottom caul plate and transferred to a single daylight press with platen temperature of  $140^\circ\text{C}$ . The press was closed at a ram pressure of 10 MPa for 10 min. After pressing, the samples were demolded and were allowed to cool at room temperature. The pressing time was selected on the basis of boil swell test (thickness swelling  $< 30\%$ ). It is observed that the surfaces of demolded boards showed no adhesion with the caul plates.

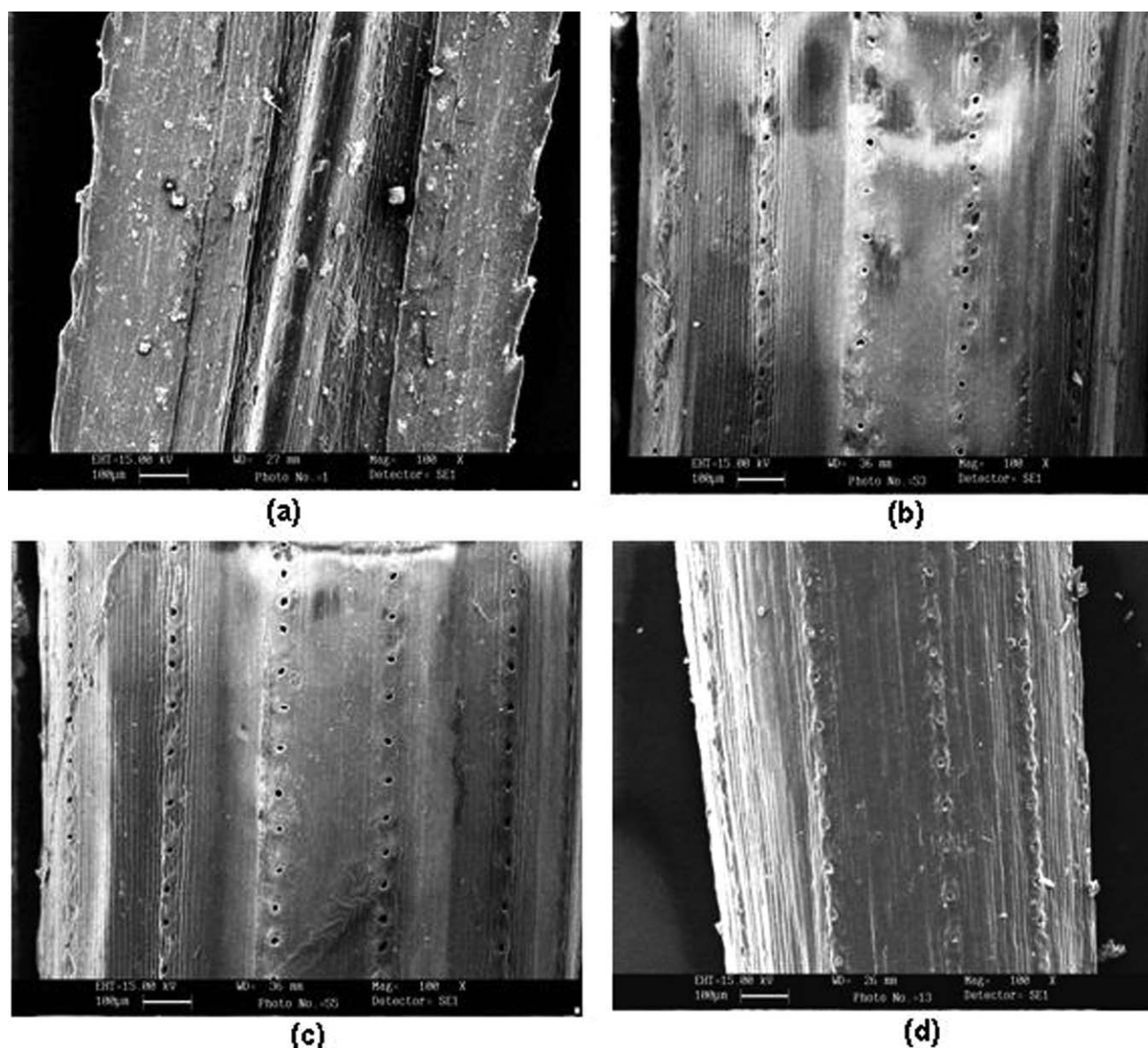
## METHODS

### Physical tests

Density and void content of the pine needle composite boards were measured as per ASTM D 792-2008 and ASTM D 2734-2009, respectively. Water absorption of samples was measured as per ASTM D 570-2005 after 2 and 24 h immersion in cold water. The tensile properties of dumbbell shaped samples-Type I were determined according to ASTM D 638-2008 at a cross-head speed of  $5 \text{ mm min}^{-1}$  on a Hounsfield Material Testing Machine (H 25 KS). The flexural properties of samples were tested at a cross-head speed of  $5 \text{ mm min}^{-1}$  and span-to-depth ratio of 16 : 1 according to ASTM D 790-2002. The internal bond strength of samples was determined by testing tensile strength perpendicular to the surface as per IS: 2380-81 at a cross-head speed of  $0.08 \text{ mm min}^{-1}$  of thickness per min.<sup>20</sup> The samples were prepared by fixing 50 mm square board to 50 mm square and 25 mm thick aluminum loading blocks with an epoxy adhesive. The screw holding test was carried out according to IS: 2380-81 at a loading rate of  $1.5 \text{ mm min}^{-1}$ . The wood screws No 8 and 50 mm length were threaded into the specimen at right angle to the face upto a half of their length in a prebore of 2.5 mm. All results were the average value of five measurements.

### Surface examination

The surface morphology of untreated and alkali treated needles was recorded on a Scanning electron



**Figure 1** SEM of untreated and NaOH treated pine needles at different treatment time like, (a) Control, (b) 30 min, (c) 60 min, and (d) 120 min.

microscope (SEM-Leo 435). Examination of split tensile fractured surfaces of both aged and unaged boards was carried out to know the failure behavior. Before SEM examination, the samples were vacuum coated with a thin film of gold/palladium to render

them conductive. Atomic force microscope (AFM NTEGRA, TS, 150) was used to measure surface homogeneity of the boards. The sample of size  $12.50 \times 8.0 \times 5.0 \text{ mm}^3$  was mounted on a metal disk, which is then held magnetically under the probe. A 100x

**TABLE I**  
Surface Energetic Properties of Untreated and Alkali Treated Pine Needles

Treatment time (min) (NaOH: 0.08 M)	Contact angle(°)		Critical surface energy ( $\text{mJ m}^{-2}$ )	Surface-free energy ( $\text{mJ m}^{-2}$ )	Polar component ( $\text{mJ m}^{-2}$ )	Dispersive component ( $\text{mJ m}^{-2}$ )
	Water	Xylene				
Control	$80.14 \pm 4.0$	$12.45 \pm 0.6$	$16.50 \pm 0.83$	$28.00 \pm 1.4$	$10.30 \pm 0.5$	$17.70 \pm 0.90$
30	$81.39 \pm 4.2$	$14.16 \pm 0.7$	$16.10 \pm 0.8$	$27.30 \pm 1.3$	$9.70 \pm 0.45$	$17.60 \pm 0.85$
60	$85.70 \pm 4.3$	$17.35 \pm 0.9$	$15.30 \pm 0.76$	$24.90 \pm 1.2$	$7.60 \pm 0.38$	$17.30 \pm 0.82$
120	$86.45 \pm 4.3$	$29.17 \pm 1.5$	$9.50 \pm 0.47$	$23.70 \pm 1.2$	$7.80 \pm 0.41$	$15.90 \pm 0.75$

Surface tension of water,  $72.8 \text{ mN m}^{-1}$ ; Surface tension of Xylene,  $18.10 \text{ mN m}^{-1}$ ; Needle diameter,  $0.87\text{--}1.09 \text{ mm}$ .

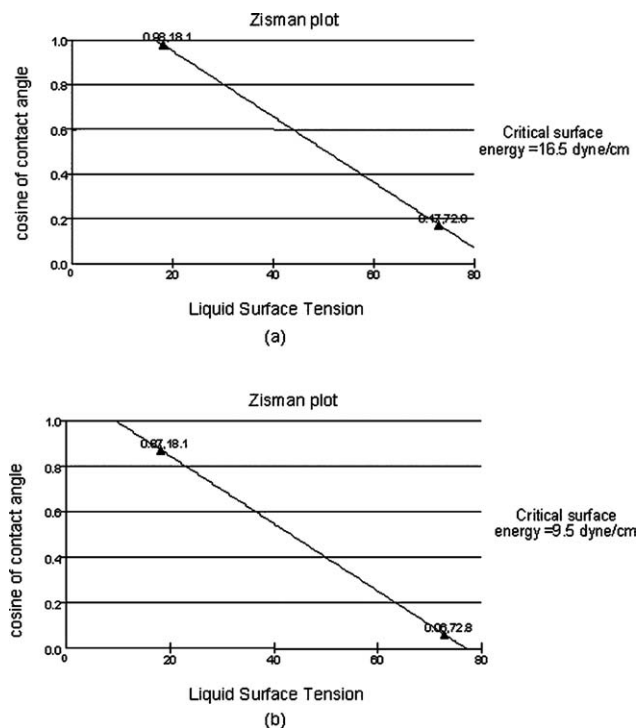


Figure 2 Zisman plots of (a) untreated pine needle and (b) alkali treated pine needle.

microscope is used to view surface texture of the samples.

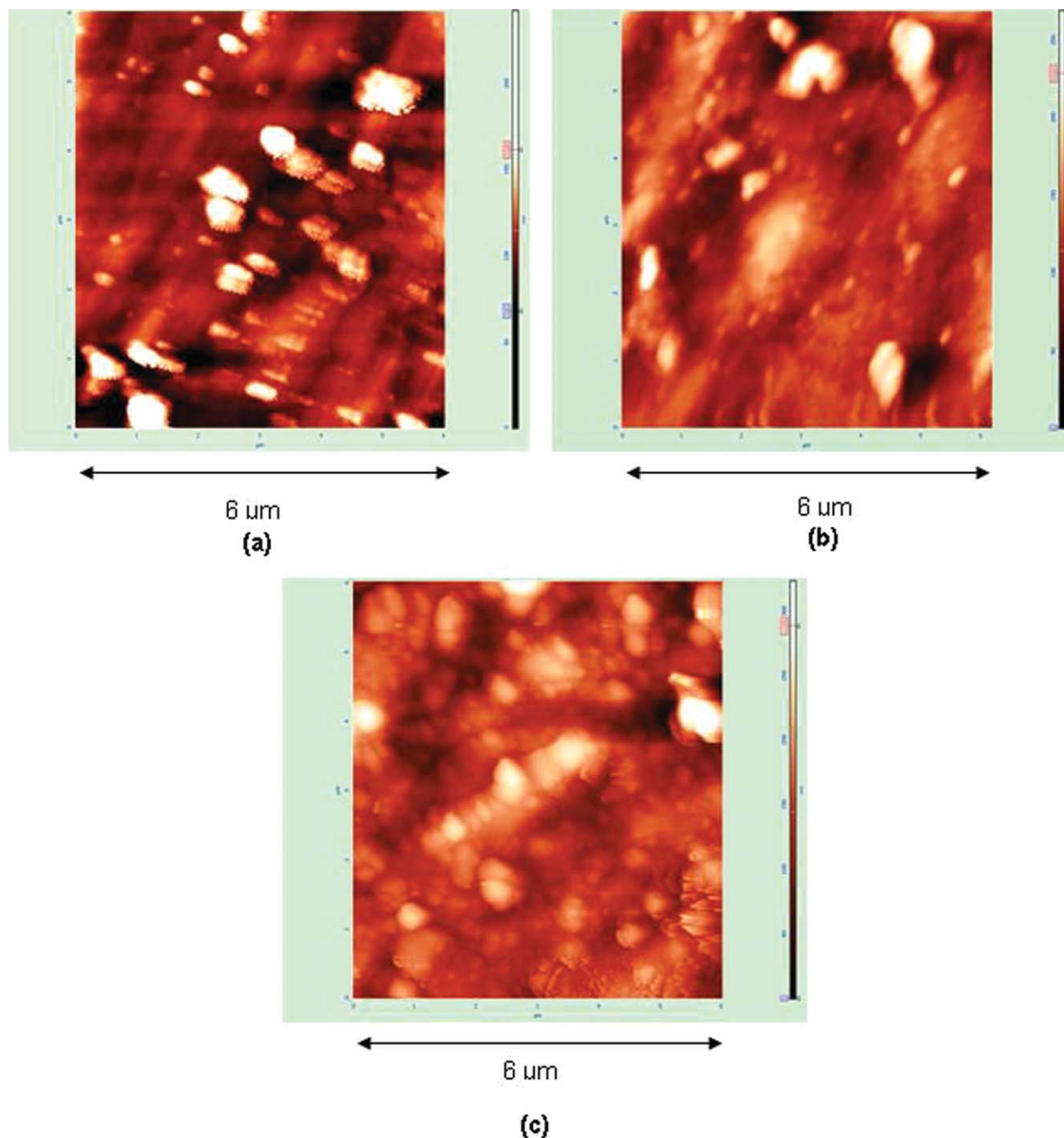
The contact angles of untreated and alkali treated pine needle surfaces were measured using sessile drop technique with the help of Dynamic contact angle analyzer (VCA Optima XE, AST Products, USA). The pine needle specimen of size 10 mm was mounted on the microscope stage and adjusted to the horizontal position. An aliquot of distilled water (0.5  $\mu$ L) was dropped onto the surface with the help of a micro syringe. A photograph was taken 10 s after the water had been dropped. AutoFAST analysis imaging

TABLE II  
Properties of Composite Boards Made from Untreated and Alkali Treated Pine Needles

Property	Untreated pine needle composite board	Alkali treated pine needle composite board
Density ( $\text{g cm}^{-3}$ )	0.90 $\pm$ 0.045	0.86 $\pm$ 0.043
Water absorption (%)		
2 h	34.81 $\pm$ 1.7	19.11 $\pm$ 0.95
24 h	79.13 $\pm$ 3.9	45.44 $\pm$ 2.2
Thickness swelling (%)		
2 h	27.11 $\pm$ 1.3	12.60 $\pm$ 0.60
24 h	47.32 $\pm$ 2.5	37.40 $\pm$ 1.8
Linear expansion 2 h soaking (%)		
Length	0.54 $\pm$ 0.027	0.19 $\pm$ 0.02
Width	0.51 $\pm$ 0.025	0.27 $\pm$ 0.03
Internal bond strength (MPa)	0.59 $\pm$ 0.029	1.12 $\pm$ 0.06
Screw withdrawal load (N)	637 $\pm$ 32	1270 $\pm$ 65

TABLE III  
Physico-Mechanical Properties of Pine Needle Composite Boards at Different Resin Adhesive Contents

Resin adhesive content (wt %)	Density ( $\text{g cm}^{-3}$ )	Void content (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Energy to break ( $\text{J} \times 10^3$ )	Internal bond strength (MPa)	Flexural strength (MPa)	Screw withdrawal load (N)	Contact angle ( $^\circ$ )
3	0.75 $\pm$ 0.035	31.87 $\pm$ 1.5	0.78 $\pm$ 0.04	323 $\pm$ 16.50	9.20 $\pm$ 0.5	0.36 $\pm$ 0.018	14.75 $\pm$ 1.4	382 $\pm$ 18	64 $\pm$ 3.2
5	0.86 $\pm$ 0.043	21.92 $\pm$ 1.1	3.33 $\pm$ 0.30	440 $\pm$ 22	82.10 $\pm$ 4.10	1.12 $\pm$ 0.06	20.20 $\pm$ 2.20	1270 $\pm$ 65	73.50 $\pm$ 3.6
7	0.91 $\pm$ 0.05	17.43 $\pm$ 1.0	5.94 $\pm$ 0.55	562 $\pm$ 28	172.20 $\pm$ 8.6	6.01 $\pm$ 0.31	25.50 $\pm$ 1.3	1350 $\pm$ 68	80.80 $\pm$ 4.0
10	0.98 $\pm$ 0.05	11.15 $\pm$ 0.5	6.24 $\pm$ 0.32	577 $\pm$ 29	194.10 $\pm$ 9.9	9.09 $\pm$ 0.5	31.08 $\pm$ 1.6	1766 $\pm$ 88	85.70 $\pm$ 4.3
15	1.06 $\pm$ 0.10	4.02 $\pm$ 0.2	8.91 $\pm$ 0.50	583 $\pm$ 30	301.20 $\pm$ 15.12	13.72 $\pm$ 1.4	44.11 $\pm$ 2.0	2138 $\pm$ 107	90.84 $\pm$ 4.5
20	1.12 $\pm$ 0.12	2.26 $\pm$ 0.11	18.23 $\pm$ 1.82	2935 $\pm$ 150	404.90 $\pm$ 20.20	28.60 $\pm$ 2.9	49.33 $\pm$ 2.5	2511 $\pm$ 125	92.95 $\pm$ 5.0



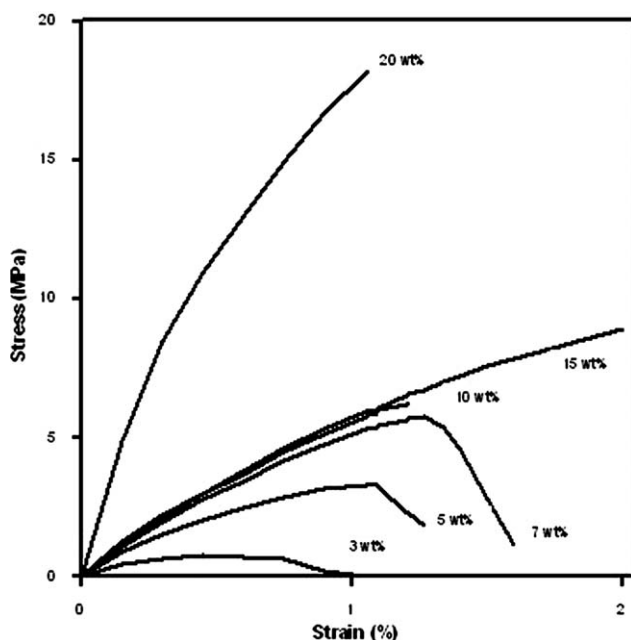
**Figure 3** AFM Images of pine needle composite boards with various resin adhesive contents, (a) 3%, (b) 5%, and (c) 7%. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

system is used to capture a droplet image and automatically calculates the contact angle with no user intervention. Five measurements were made for each sample. Surface energy software (SE-2500) was used for calculation of critical surface energy of untreated and alkali treated pine needles using Zisman plots.

#### Accelerated aging test

The samples were exposed to various relative humidity (75% RH, 98% RH, and 98% RH at 50°C) and

immersion in cold water for 60 days. The relative humidity was maintained in a desiccator according to the method described in ASTM C 427-64. Weight gain and thickness swelling of the exposed samples were recorded at a regular interval of time. The internal bond strength of samples was determined by exposing them under accelerated water aging and cyclic aging according to IS: 12,406-2003.<sup>21</sup> Under accelerated aging, the samples were subjected to immerse in cold water and water is brought to boiling and kept at boiling temperature for 2 h followed



**Figure 4** Tensile stress-strain curves of pine needle composite boards as a function of various resin adhesive contents.

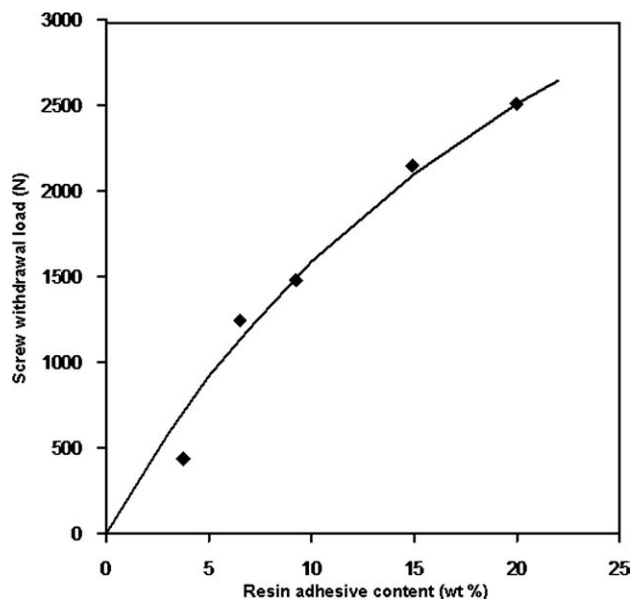
by cooling in water. In cyclic aging, the samples were immersed in water at  $27 \pm 2^\circ\text{C}$  for a period of 72 h followed by drying in air at  $27 \pm 2^\circ\text{C}$  for 24 h and then kept at  $70^\circ\text{C}$  for 72 h. The cycle was repeated thrice as mentioned in the Standard. The aged samples were examined for dimensional changes and internal bond strength.

## RESULTS AND DISCUSSION

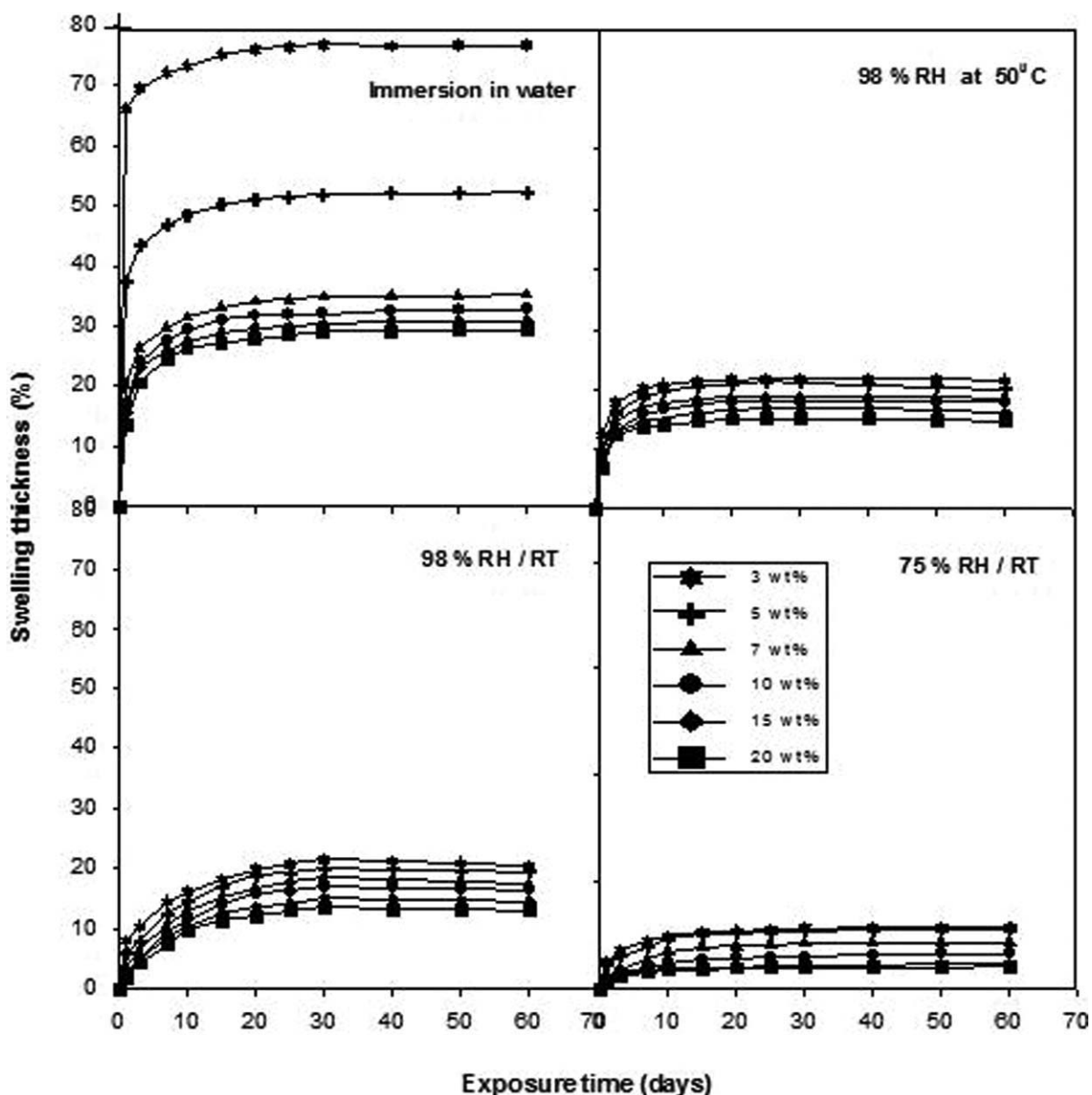
### Effect of alkali treatment

Figure 1 shows SEM of the untreated and alkali treated pine needles. The surface of untreated pine needles is smooth and fully covered with a thick waxy cuticle layer that may inhibit their adequate bonding with resin adhesive [Fig. 1(a)]. However, the alkali treated needles showed a rough surface with clear fibrillar and less compact structure because of swelling [Fig. 1(b-d)]. The progressive destruction of surface waxy layer from the needles along with partial removal of noncellulosic constituents such as lignin, hemicellulose, and extractives occurred with increasing treatment time. The needles lost 15% of these materials after 2 h treatment leading to better separation of the individual cells/ thinner fibers. This needle fibrillation increases the effective surface area available for wetting by the resin adhesive. The improvement in the wettability of these treated needles can be explained on the basis of contact angle data (Table I). The differences in the surface analysis of untreated and alkali treated needles are visible. Unexpectedly, the higher contact angle of treated needles

may consider mainly because of poor liquid flow over the rough surface as observed in SEM to fill completely every cell cavity, pore, or crevice. Because of this, wettability of the needles was characterized by measuring a critical surface tension through Zisman's rectilinear relationship between surface tension and cosine contact angle (Fig. 2). The 2 h alkali treated needles had a lower critical surface tension ( $9.5 \text{ mJ m}^{-2}$ ) than the untreated ones ( $16.5 \text{ mJ m}^{-2}$ ) showing their superior surface wettability. The physical meaning of critical surface tension is that surface tension below which a liquid will completely wet the solid.<sup>22</sup> It is found that pine needle behaves as low energy surface ( $28 \text{ mJ m}^{-2}$ ) as compared with the wood ( $56\text{--}97.6 \text{ mJ m}^{-2}$ ). The surface-free energy of pine needles was reduced by 15% after 2 h alkali treatment. The reduced polar component of surface-free energy of these treated needles indicates superior spreading of adhesive onto their surfaces as compared with control samples. In the case of untreated pine needles, poor wettability may interfere with the spreading and penetration of resin adhesive, thereby affecting the bond formation between the resin adhesive and needles. On alkali treatment, the emergence of fibrillar and rough morphology is believed to provide good bonding with the resin adhesive and consequently, to improve strength and dimensional stability of the composite boards. This can be explained on the basis of properties of untreated and alkali treated needle composite boards (Table II). Under immersed water for 2 h and 24 h, the alkali treated pine needle boards exhibited less water absorption (43–45%) and thickness swelling (21–54%) than the water absorption and thickness swelling of untreated pine needle boards. The linear expansion of alkali treated pine needle



**Figure 5** Screw withdrawal load of pine needle composite boards as a function of resin adhesive contents.



**Figure 6** Thickness swelling of pine needle composite boards as a function of exposure time under different humidity and when immersed in water.

boards is also 2–3 times less than that of untreated boards showing their superior dimensional stability. The cohesion of interparticles in the untreated needle boards is also insufficient in terms of internal bond strength. Its internal bond (split tensile strength) was reduced by 90% compared with alkali treated boards. The withdrawal resistance of screws of untreated needle boards was also 95% less than the alkali treated needle boards along with embossing at the point of screw withdrawal.

#### Properties of composite boards

The physico-mechanical properties of composite boards are shown in Table III. It is observed that boards properties improve with increasing quantities

of prepolymer resin adhesive. The presence of polyol in the isocyanate prepolymer may inhibit penetration of isocyanate into inner cavities of needles keeping it more available for interparticle adhesion<sup>10</sup> and consequently, the improvement in the strength of composite boards. Evidence of this adhesion phenomenon can be viewed on AFM images of the finished board surfaces where both bonded and debonded regions coexist (Fig. 3). At low-resin adhesive content (3%), decohesion of particles was dominant onto surface whereas at higher resin adhesive content, a smooth surface morphology was observed in which particles are well bonded. It is noted that dimensions of the smooth region increase with increasing resin adhesive content. The uniformity in the distribution of particles clearly indicates

TABLE IV  
Dimensional Stability of Pine Needle Composite Boards

Resin adhesive content (wt %)	Water absorption (%)		Thickness swelling (%)		Linear expansion (length) (%)		Equilibrium moisture content (%)			
	2 h	24 h	2 h	24h	2 h	2 h	75 % RH	98% RH	98% RH	98% RH 50°C
3	37.7 ± 1.8	77.01 ± 3.8	29.79 ± 1.5	66.02 ± 3.2	0.22 ± 0.01	6.60 ± 0.38	26.01 ± 1.3	25.30 ± 1.2	96.5 ± 5.0	
5	19.1 ± 0.95	45.44 ± 2.2	12.60 ± 0.6	37.40 ± 1.8	0.19 ± 0.02	4.90 ± 0.25	23.06 ± 1.2	22.10 ± 1.1	79.02 ± 4.0	
7	10.20 ± 0.5	37.70 ± 1.8	7.80 ± 0.4	20.30 ± 1.1	0.093 ± 0.005	4.20 ± 0.21	19.60 ± 0.95	19.20 ± 0.95	64.20 ± 3.2	
10	5.54 ± 0.25	22.70 ± 1.1	3.40 ± 0.17	16.80 ± 0.80	0.082 ± 0.004	3.00 ± 0.15	18.60 ± 0.9	17.10 ± 0.80	58.00 ± 3.2	
15	3.70 ± 0.19	14.70 ± 0.7	3.10 ± 0.15	15.70 ± 0.75	0.079 ± 0.004	2.19 ± 0.12	17.90 ± 0.85	16.40 ± 0.82	44.20 ± 2.2	
20	2.50 ± 0.12	9.93 ± 0.45	2.50 ± 0.12	13.70 ± 0.68	0.068 ± 0.003	2.00 ± 0.10	17.50 ± 0.8	16.01 ± 0.80	38.50 ± 1.90	

adequate spreading of binder onto particle surfaces as evidenced also in their low surface-free energy value during contact angle measurement. Because of good spreading, resin availability even at low-level is sufficient to wet out the needle furnishes during intense mixing with resin adhesive. The composite boards containing 3–7% resin adhesive content belong to medium density particle boards category (0.7–0.9 g cm<sup>-3</sup>) as per IS: 3087-2005.<sup>23</sup> It is observed that increase of resin adhesive content increases density and reduces void content of the composite boards. The boards with 3% resin adhesive contain 31.87% void content. The presence of excessive voids reduces board's mechanical properties.<sup>24</sup> They absorb water more readily causing development of swelling stresses at the interface, the consequent resin microcracking and loss of properties upon partial drying.

The difference in the slope of the tensile stress-strain curves of composite boards can be explained on the basis of interparticle adhesion (Fig. 4). In the case of low-resin adhesive content boards, lack of knee point in the curves demonstrates synergistic involvement of needle furnish and resin adhesive in the load carrying process, whereas the initial load in the higher resin adhesive content boards was carried out by resin alone showing a demarcated knee point. The tensile and flexural strengths of composite boards increased as the resin adhesive content was increased. This could be attributed to the good interparticle adhesion which in turn, provides better efficiency of stress transfer between needle furnish and resin adhesive. The isocyanate prepolymer applied onto needle furnish reacts with hydroxyl groups of lignocellulosics to form urethane bonds in the process of pressing. Additionally, this improvement is also supplemented to the formation of cross-linked interpenetrating network following the reaction between moisture and isocyanate that contributes to the panels mechanical strength. The marginal change in the tensile modulus of composite boards was noticed except in the case of 20% resin adhesive content boards. Energy to break of the boards showed an increasing trend as the resin adhesive content was increased. The adequate interparticle adhesion creates satisfactory interfacial regions, which may inhibit frictional pull-out of needle fiber bundles from the resin adhesive. This, in turn improves the ability of the composite boards to absorb more energy during fracture propagation. The withdrawal resistance of screws from the face panel increases from the low-resin adhesive content boards to the high-resin adhesive content boards (Fig. 5). Embossing was common in all the samples at a point of screw withdrawal. Increasing the resin adhesive content from 3–5% resulted in boards of sufficient screw withdrawal load to pass the requirement of IS: 3087-2005.



**TABLE V**  
**Effect of Wax Content on the Dimensional Stability of the Pine Needle Composite Boards**

Property	Pine needle boards			
	Control		Wax containing boards	
	3%	5%	3%	5%
Water absorption (%)				
2 h	37.77 ± 1.8	19.11 ± 0.95	12.43 ± 0.60	9.11 ± 0.5
24 h	77.01 ± 3.8	45.44 ± 2.20	44.7 ± 2.20	31.21 ± 1.5
Thickness swelling (%)				
2 h	29.79 ± 1.5	12.60 ± 0.60	11.60 ± 0.55	7.84 ± 0.4
24 h	66.02 ± 3.2	37.40 ± 1.8	47.77 ± 2.8	40.73 ± 2.6
Surface absorption (%)				
2 h	10.81 ± 0.50	3.70 ± 0.03	4.02 ± 0.22	2.70 ± 0.14
24 h	37.56 ± 1.90	17.10 ± 0.90	21.96 ± 1.1	14.15 ± 0.75
Linear expansion (%)				
2 h	0.22 ± 0.01	0.19 ± 0.02	0.10 ± 0.005	0.02 ± 0.002
24 h	1.02 ± 0.10	0.94 ± 0.045	1.30 ± 0.10	0.69 ± 0.04
Internal bond strength (MPa)	0.36 ± 0.018	1.12 ± 0.06	0.28 ± 0.015	0.89 ± 0.045

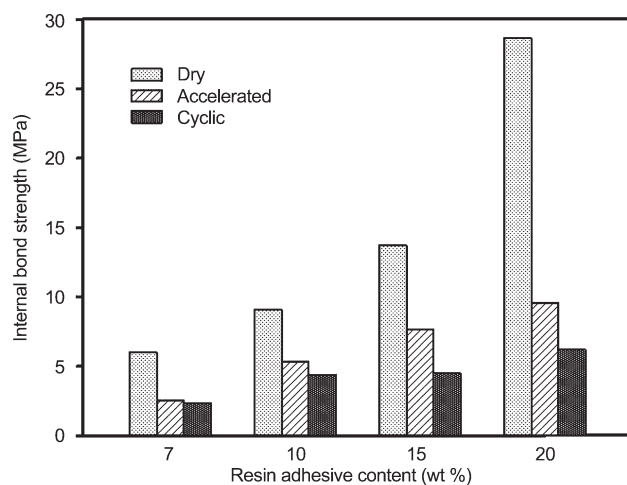
The high resin adhesive content boards possess screw holding power comparable with conventional timber according to Indian National Building Code 2005, Sec 3.

#### Effect of accelerated aging

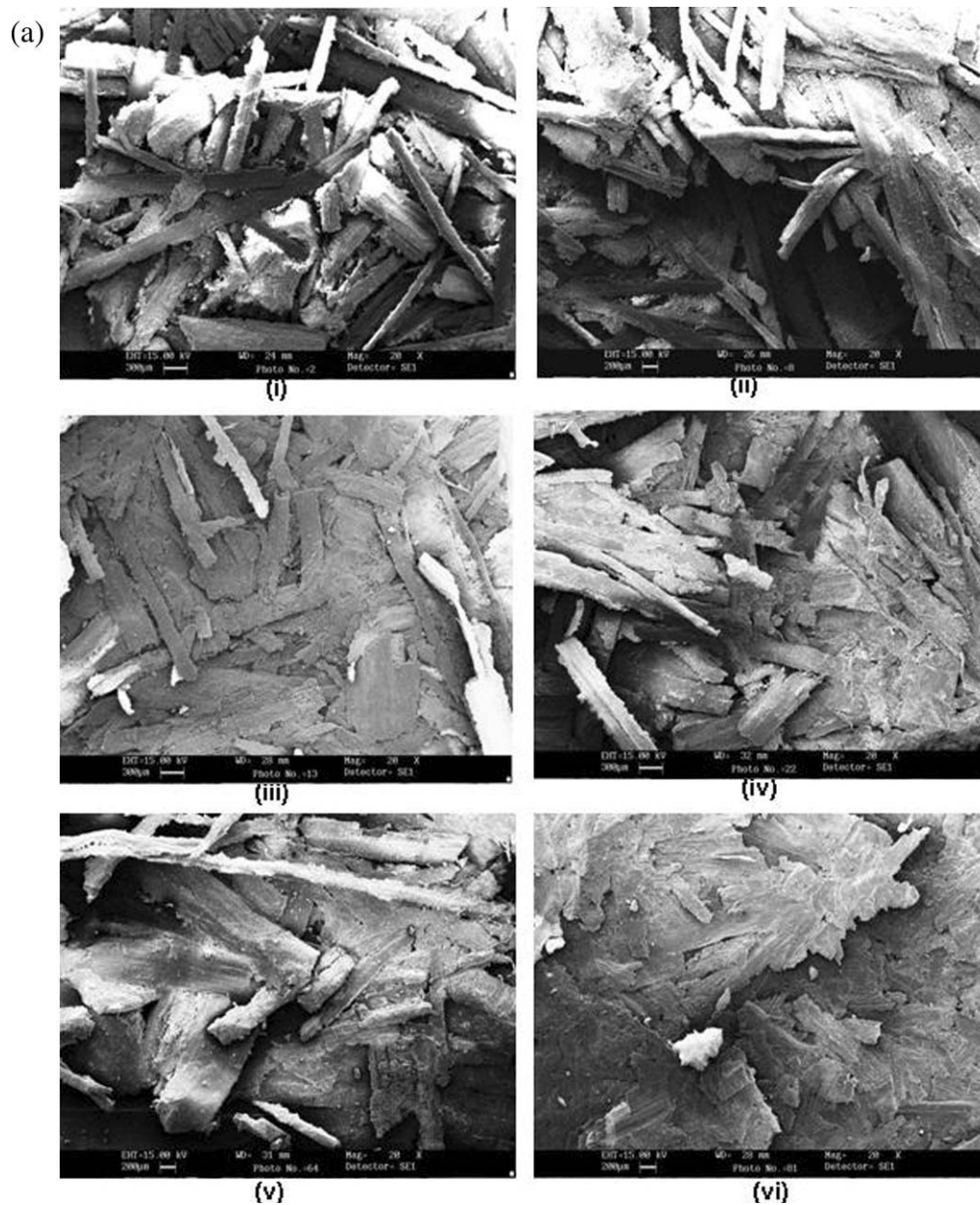
Figure 6 shows thickness swelling of the composite boards under different humidity and when immersed in water. During exposure, the thickness swelling increased rapidly, and then it leveled off (15–20 days). But a further increase of exposure, the samples experienced insignificant swell variations. The equilibrium moisture content of composite boards increases with increasing humidity levels. At low-humidity, the variation in thickness swelling was found to be 2–7% only at equilibrium moisture content whereas at higher humidity levels, the samples exhibited these changes ranged between 13–23%. Compared with 98% RH, a decrease in the dimensional changes at 98% RH at 50°C is considered mainly because of the formation of cross-linked interphase by the post curing of the resin adhesive binder at 50°C. It is observed that the composite boards swelled in immersed water 2–3 times as much as the samples exposed to 98% RH because of less stable bonds formed at the interface in presence of water by the reaction between isocyanate and hydroxyl groups of needles.

As expected, increase of resin adhesive content reduces thickness swelling, linear expansion, and water absorption of the composite boards (Table IV). The low-resin- adhesive bonded boards exhibited high-water absorption and thickness swelling after 2 h and 24 h water soaking and do not meet commercial Standard requirements. These boards also quickly absorbed surrounding moisture and warped. This adverse effect might be attributed to the insuffi-

cient bond between needle furnish. As a result, many gaps/voids occur in the boards that allow water to enter resulting in large swelling and water absorption. The addition of 1% paraffin wax in the composite board formulation (3% resin adhesive content) reduces 61.06% thickness swelling and 67.03% water absorption respectively after 2 h water soaking (Table V). The corresponding linear expansion of the boards was 0.1%. The surface absorption was also reduced significantly when wax is added in the board formulation. The internal bond strength of the composite boards containing 5% resin adhesive content was reduced by 20% after adding paraffin wax in the formulation. This suggests that the wax interfered with isocyanate resin adhesive bonding during pressing resulting in reduced bond quality. It is also reported that thickness swelling of the particle boards depend on their density. High-density boards exhibited 4–8% more thickness swelling than the low-



**Figure 7** Internal bond strength of pine needle composite boards under dry and wet conditions.



**Figure 8** (a) SEM of split tensile surface of unaged pine needle composite boards with various resin adhesive contents: (i) 3% (ii) 5% (iii) 7% (iv) 10% (v) 15% (vi) 20%, (b) SEM of split tensile surface of pine needle composite boards with various resin adhesive contents under cyclic aging (i) 7% (ii) 10% (iii) 15% (iv) 20%, and (c) SEM of split tensile surface of pine needle composite boards with various resin adhesive contents under accelerated water aging (i) 7% (ii) 10% (iii) 15% (iv) 20%.

density boards. This difference is mainly because of the release of greater compression stress at a later stage in the high-density boards.<sup>25</sup> Increasing resin adhesive content level from 3 to 5%, the composite boards passed the tests. The thickness swelling and water absorption reduced from 29.80 to 12.60% and 37.70 to 19.11% respectively after 2 h soaking in water and this is attributed to the good needle furnish-resin adhesive bonding. The composite boards with 5% resin adhesive content satisfied water absorption requirement prescribed in the standard after 24 h soaking. The contact angle of the composite boards

was increased from 64° for 3% resin adhesive to 92.95° for 20% resin adhesive content. This indicates that the boards have adequate surface moisture probably due to availability of unreacted isocyanate groups.<sup>26</sup> Their higher moisture content at the surface may encourage greater surface plasticization, which resulted in less water absorption and hence better dimensional stability of the boards.

The internal bond strength of the fresh and the aged composite boards is shown in Figure 7. It is noticed that, the location of the plane of failure occurs mainly in the upper or middle line of the

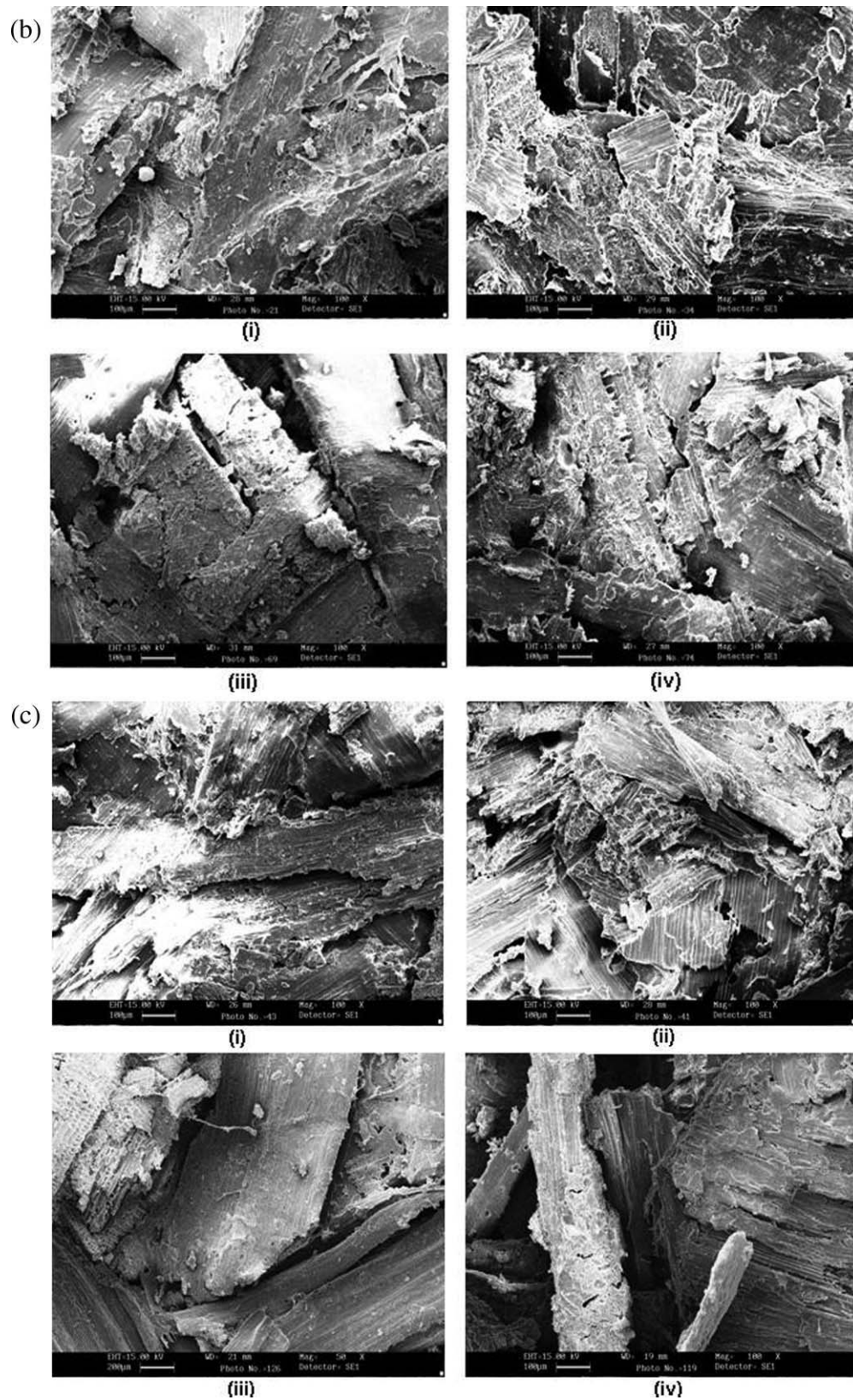


Figure 8

board thickness. The internal bond strength increased significantly with an increase of resin adhesive content in the boards. To know cohesion of

the panels, the samples were aged in accelerated water and cyclic (alternate wetting and drying). Under cyclic aging, reduction in the internal bond

**TABLE VI**  
**Properties of Pine Needle Composite Boards as per IS:**  
**3087–2005 / EN 312**

Property	Standard Specification		Pine needle composite board (~ 5% resin adhesive content)
	IS: 3087	EN 312	
Density variation (%)	± 10	-	± 0.9
Water absorption (%)			
2 h Soaking	25	-	19.11 ± 0.95
24 h Soaking	50	-	45.44 ± 2.20
Linear expansion 2 h Soaking (%)			
Length	0.5	-	0.19 ± 0.02
Width	0.5	-	0.27 ± 0.03
Thickness swelling 2 h water soaking (%)	10	16	12.6 ± 0.6
Modulus of rupture (N mm <sup>-2</sup> )	11	14	20.20 ± 2.20
Tensile strength perpendicular to surface (N mm <sup>-2</sup> )	0.8	0.28–0.45	1.12 ± 0.060
Screw withdrawal strength Face (N)	1250	-	1270 ± 65

strength was between 54–78% whereas in accelerated water a decrease in strength ranged between 41–67%. The severity of cyclic aging effect was more than that of an accelerated water aging. The high-resin adhesive content boards experienced more strength loss during cyclic (21%) and accelerated water (8%) than that of the low-resin adhesive content boards. The low-resin adhesive content bonded boards (<5%) possess insignificant internal bond strength after both cyclic and accelerated water aging. As expected, cohesive loss in the boards affected considerably by the combined action of water and temperature. SEM micrographs of split tensile surfaces of the control and the aged samples are shown in Figure 8(a–c). In the case of unaged samples, the split surface of low-resin bonded boards consists of unbonded pulled-out fibers whereas higher resin adhesive content boards exhibited smooth cohesive failure surfaces dominated with embedded fibers. At some places, splitting of needle furnish is also viewed because of the existence of strong interfacial regions and also inherent weakness of needle furnish itself. Under cyclic exposure, the split surfaces showed a loosen texture in which swelled and pulled out needle furnishes were observed. The splitting of needle furnishes, and their breakage was also noticed contrary to the unaged samples [Fig 8(b)]. In the case of accelerated water aging, the split surface exhibited relatively more swelled, pulled out fibers with fractured/ breakage surfaces than that of cyclic aging [Fig. 8(c)]. However, it is surprisingly noticed that the composite boards retained more internal bond strength after accelerated water aging than the samples aged to

cyclic exposure. The debonded regions developed in cyclic aging are caused by expansion and contraction of the needle furnishes because of water absorption/desorption during wetting and drying stages. It is also reported that a high content of water soluble substances leached during immersion in hot water led to the initiation of debonding between the fiber and the matrix via creation of an osmotic pressure at the fiber surface. This has resulted in an early mechanical failure of samples.<sup>27</sup>

A comparison was made between properties of the isocyanate prepolymer bonded pine needle boards and the commercial resin bonded wood/lignocellulosic particle boards<sup>23,28</sup> (Table VI). The composite boards at 5% resin adhesive level exhibited 40% higher internal bond strength than the specified value of the Standard for phenolic/urea bonded boards because of its superior adhesive properties even at low-resin content. The screw withdrawal load was comparable with the commercial particle boards. The water absorption of the pine needle boards is 23.56 and 9.12% less than the phenolic/urea bonded boards after 2 and 24 h soaking. On contrary, thickness swelling of the pine needle boards after 2 h water immersion is 26% higher than the commercial resin bonded boards. After adding paraffin wax (1%), the thickness swelling in the boards is reduced from 12.62 to 7.84% (37.88%), which pass the requirement of the commercial Standard. Linear expansion of the pine needle boards is also 80% less than that of phenolic/urea bonded boards after 2 h water immersion.

## CONCLUSIONS

The results indicate that mercerized pine needle furnishes bonded with isocyanate prepolymer can be used as panel products for wood substitute application in buildings. In making composite boards, it is desirable to use wettable needle furnishes for their good bonding with resin adhesive. The prepared boards/panels at 5% resin adhesive content level satisfy the exterior grade requirements of IS: 3087-2005 / EN 312-2003 in terms of physico-mechanical properties and dimensional stability. At low-resin adhesive content, use of hydrophobic compound is necessary in the board formulations to achieve desired dimensional stability to meet the Standard requirements. Under wet conditions, loss in the strength and dimensional stability can be minimized by the use of isocyanate prepolymer with an optimum level of equivalent ratios within which the polyol can interact with the isocyanate to produce a strong bond by cross-linking. Blending of needle furnishes with other fibers at low-isocyanate prepolymer content would probably produce a strong composite board suitable for outdoor use especially in

moist places. Work is continued on decay resistance and flammability behavior of composite boards.

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